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Purification of Vegetable Tannins

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It has been clearly demonstrated recently that vegetable tanning extracts are complex mixtures of tannins and non-tannins [1]. In the study of the physical and chemical properties of these naturally occurring vegetable tannins, it is important to obtain the tannins in a high state of purity. Various general methods for purifying the tannins have been previously employed [2, 6]. These methods include: (1) Adsorption of tannins by hide powder, (2) Precipitation of the tannins with lead acetate, (3) Salting out of aqueous solution by sodium chloride, and (4) Purification through the use of various organic solvents.

The use of organic solvents for purifying the vegetable tannins appears to merit investigation for developing a satisfactory method for obtaining tannins in a high state of purity. Previous workers have employed organic solvents for this purpose, but in general the results have been highly empirical and it has been necessary to resort to mixtures of solvents to accomplish this purpose [5, 6]. More suitable organic solvents for purifying tannins are needed. Because of certain properties methyl ethyl ketone seemed to merit investigation.

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Methyl ethyl ketone is partially miscible with water; and the properties of methyl ethyl ketone-water mixtures, particularly the fact that this ketone at equilibrium dissolves water to the extent of 12.6% by weight, suggested that this solvent may be generally useful for purifying vegetable tannins. The results of such an investigation are reported in this paper.

Experimental

The crude canaigre extract was obtained by batchwise leaching of canaigre roots with a 50% acetone-water solution as described previously[7]. Tannic acid was obtained by leaching Chinese gall nuts with water. The other extracts studied were the commercially available extracts.

Purification by Liquid-Liquid Extraction with Methyl Ethyl Ketone

The procedure described below is typical of the method used for purifying the various extracts. The crude, dry extract was dissolved in water to give solutions of 25% by weight (solids content). The aqueous solution was extracted in a separatory funnel five times with methyl ethyl ketone which had previously been saturated with water. The volume ratio of solvent to aqueous liquor was 1.0 for the first extraction and 0.5 for subsequent extractions. The methyl ethyl ketone layers were combined and evaporated to dryness in a vacuum still heated by steam, the final stage of drying being carried out at a pressure of approximately 1.0 mm of mercury. The residual solid was ground, and the tannin content determined by the Official Method of the American Leather Chemists Association[8].

In a few cases difficulty in separating the two liquid phases was encountered in the first stage of extraction. This difficulty was generally overcome by filtering the mixture through a small plug of cotton or by centrifuging the mixture. In the case of quebracho extract the insolubles which separated from the hot aqueous solution on cooling were removed by decantation prior to extraction with methyl ethyl ketone.

The results obtained in the purification of aqueous solutions of various tannins with methyl ethyl ketone saturated with water are shown in Table I. In the case of canaigre tannin substantially the same results were obtained whether dilute solutions, 10% solids liquor, or more concentrated solutions, 50% solids or the solid extract, were used. The results obtained with other solvents are shown in Table II. Considerable difficulty in separating the two liquid layers was encountered in the extractions using methyl isobutyl ketone as the solvent.

The "apparent" distribution of canaigre tannin between water and methyl ethyl ketone was determined as follows: equal volumes of an aqueous solution of the tannin and water saturated ketone were shaken, the organic layer separated and the solvent evaporated. The solid extract was analyzed for

TABLE I

Purification of Tannins by Liquid—Liquid Extraction with Methyl Ethyl Ketone

Tannin	Analysis of Extract %												
	Crude Extract						Refined Extract						
	Total solid	Soluble solid	Insol.	Non Tannin	Tannin	Purity*	Total solid	Soluble solid	Insol.	Non Tannin	Tannin	Purity*	Tannin Recovery %
Canaigre†	94.5	94.4	0.1	47.1	47.3	50.1	87.7	87.7	0.0	8.5	79.2	90.3	88
Wattle bark	91.1	88.9	2.2	23.1	65.8	74.0	100.2	99.5	0.7	5.7	93.8	94.2	65
Quebracho	86.5	80.7	5.8	7.9	72.8	90.2	96.0	92.7	3.3	4.4	88.3	95.3	58
Sulfited quebracho	92.0	91.5	0.5	15.7	75.8	82.9	96.5	95.4	1.1	6.7	88.7	93.0	56
Myrobalans	95.0	91.6	3.4	33.0	58.6	64.0	96.7	95.7	1.0	11.4	84.3	88.1	79
Tannic acid	97.8	96.0	1.8	14.5	81.5	84.9	96.5	94.5	2.0	8.0	86.4	91.6	90
Divi Divi‡	25.7	24.2	1.5	12.6	11.6	47.9	96.6	92.9	3.7	18.1	74.7	80.5	68
Cube Gambier	90.8	49.7	41.1	32.0	17.7	35.6	98.1	93.5	4.6	29.7	63.8	68.2	97
Plantation Gambier	92.4	85.7	6.7	37.1	48.6	56.7	88.6	84.5	4.1	26.1	58.4	69.1	80
Hemlock bark‡	27.9	27.5	0.4	7.3	20.2	73.6	94.3	86.9	7.4	10.3	76.6	88.1	39
Valonia	91.0	89.5	1.5	25.6	63.9	71.4	97.6	84.6	13.0	18.9	65.7	77.7	15
Chestnut	92.5	91.7	0.8	29.8	61.9	67.5	96.9	93.8	3.1	24.9	68.9	73.4	20
Borneo cutch	76.1	73.6	2.5	16.8	56.8	77.2	97.4	92.0	5.4	9.0	83.0	90.2	18
Mangrove bark	88.3	87.9	0.4	21.8	66.1	75.2							<8

*Purity = % Tannin/% Sol. solids x 100.

†a 50% solids content liquor was extracted. Total sugar (as glucose): in crude, 36.4%; in refined, 4.3%.

‡analysis of the crude based on a 25° Twaddell liquor.

tannin content and the "apparent" distribution calculated. The results are shown in Table III.

TABLE II

Purification of Tannins with Other Organic Solvents*

Tannin	Solvent	Purity ** % Crude	Refined	Tannin recovery, %
Canaigre	Sec. -Butyl alcohol	47.7	68.4†	67
Canaigre	tert. Amyl alcohol	50.1	74.8‡	52
Canaigre	Methyl isobutyl Ketone	47.7	90.6	33
Tannic acid	" " "	84.9	93.2	85
Plantation Gambier	" " "	56.7	66.0	53
Wattle	" " "	74.0	90.8	18
Myrobalans	" " "	64.0	87.6	22
Divi Divi	" " "	54.6	70.8	17
Cube Gambier	" " "	35.6	59.8	47
Quebracho	" " "	90.2	93.5	29
Sulfited quebracho	" " "	82.9	93.9	25
Chestnut	" " "	67.5	57.8	7

* Extraction of liquors from Mangrove, Valonia and Borneo cutch with Methyl isobutyl ketone resulted in very low tannin recovery (< 4%).

$$**\text{Purity} = \frac{\%\ \text{tannin}}{\%\ \text{Sol. solid.}} \times 100$$

†Total sugar (as glucose): in crude, 37.4%; in refined, 20.3%.
‡Total sugar (as glucose): in crude, 36.4%; in refined, 16.4%.

TABLE III

Apparent Distribution of Canaigre Tannin between Methyl Ethyl Ketone (MEK) and Water

Treatment	Phase, ml, H_2O	MEK	Solid in MEK, g.	Tannin %	Purity %	K=Cs/Cw*	Extraction eff., %†
10% Canaigre‡—1st extraction	550	270	14.5	90.6	93.2	4.05	66.5
2nd extraction	555	550	4.1	82.1	84.0	1.37	17.1
3rd extraction	550	535	1.2	—	—	—	—
25% Canaigre‡—1st extraction	174	131	17.8	90.6	91.3	5.95	81.8
2nd extraction	174	170	2.1	76.1	78.6	0.82	8.1
50% Canaigre‡—1st extraction	55	82	21.2	84.5	84.9	6.25	90.8
2nd extraction	56	47	0.9	—	—	—	—

*On tannin content basis; Cs = concentration of tannin (g/ml), as determined by hide powder, in MEK phase; Cw = concentration of tannin (g/ml.) in H_2O phase (by difference).
†Extraction efficiency = tannin in MEK/total tannin in crude X 100.
‡Analysis of solid crude canaigre: TS, 96.7; SS, 96.8; Tan., 46.1; Non-tan., 50.7; purity, 47.7. In each case the aqueous solution contained 42.8 g. of solid extract.

Leaching of Tannins from Plants with Methyl Ethyl Ketone-Water Azeotrope

The finely divided plant material, 25 to 50 g., was placed in the thimble of a Soxhlet apparatus. A mixture of methyl ethyl ketone and water (generally 250 ml. of ketone and 75 ml. of water) was refluxed in the still pot of the

Soxhlet, and the semi-continuous leaching of the plant source of tannin was continued until extraction appeared complete (10 to 20 hours). Both the solvent and aqueous layers in the still pot were transferred to a vacuum still heated by steam where solvent and water were evaporated, the final stages of drying being conducted at a pressure of approximately 1 mm. of mercury. The residual solid was ground and analyzed according to the Official Method of the ALCA. The results are shown in Table IV. In the case of canaigre

TABLE IV

Leaching of Tannins from Plant Source with Methyl Ethyl Ketone—Water Azeotrope

		Analysis of Extract, %					
Tannin Source	Tannin recovery, %	Total solids	Soluble solids	Ins.	Non-Tannin	Tannin	Purity*
Sumac leaves (Sicilian)	96	48.9**	41.5**	7.4**	9.5**	32.0**	77.2
Gallnuts (Chinese)	88	91.9	89.4	2.5	8.8	80.6	90.1
Canaigre roots (shredded)	69	97.6	93.7	3.9	23.7	70.0	74.7
Canaigre roots (powdered)†	46	93.6	89.6	4.0	7.8	81.7	91.3
Canaigre roots (powdered)‡	80	96.3	90.2	6.1	6.9	83.3	92.3
Wattle bark	87	93.6	88.5	5.1	9.3	79.3	89.5
Hemlock bark	82	97.2	76.4	20.8	23.0	53.4	69.9

*Purity $= \frac{\%\text{tannin}}{\%\text{ sol. solid}} \times 100$

**The tannin was obtained in aqueous medium

†Leaching appeared to occur mainly at the outer portion of the canaigre root mass.

‡Leaching conducted in vacuum, Soxhlet apparatus maintained at a pressure of 250–350 mm. of Hg.; temperature of the refluxing methyl ethyl ketone–water azeotrope was 50 to 53° C.

better results were obtained when the leaching was conducted at reduced pressure (250 – 350 mm.), the boiling point of the methyl ethyl ketone-water azeotrope being reduced from 73° C. to approximately 50–55° C.

Discussion

Methyl ethyl ketone is a relatively low-cost, commercially available organic solvent which is partially miscible with water. At room temperature the solvent layer of the two phase system of methyl ethyl ketone and water contains 12.6% by weight of water and 87.4% by weight of methyl ethyl ketone [9]. Thus it would appear that this solvent may be of value for purifying tannins by liquid-liquid extraction of aqueous tannin solutions, and such was found to be the case. Because of the low tannin recoveries this solvent was not useful with valonia, chestnut, Borneo cutch, and mangrove extracts. The purity of all the vegetable tannins investigated, excepting mangrove bark extract, was considerably improved. Extracts of purity ranging from 88 to 95% were obtained in the batchwise liquid-liquid extraction of quebracho, sulfited quebracho, wattle, canaigre, myrobalans, tannic acid, and hemlock tannins. The purity of the extracts was not quite so high, approximately

70–80%, when this method of purification was applied to divi-divi and gambier extracts. Recovery of tannin amounted to 80% or better in the case of canaigre, myrobalans, tannic acid, cube gambier, and plantation gambier. Tannin recoveries in the range of 40 to 65% were obtained with wattle, quebracho, sulfited quebracho, and hemlock bark extracts. It would be expected that higher extraction efficiency would result from continuous countercurrent liquid-liquid extraction than from batchwise extraction. The use of methyl isobutyl ketone in place of methyl ethyl ketone gave satisfactory results only in the case of tannic acid, from which 85% of the tannin was recovered in a state of purity of 93%. In general, excepting tannic acid and the gambiers, very low tannin recoveries were observed using methyl isobutyl ketone as a solvent in liquid-liquid extraction, and this solvent does not appear to be as promising as methyl ethyl ketone for purifying the tannins. Secondary butyl alcohol and tertiary amyl alcohol, which are also partially miscible with water, were considerably less selective and efficient than methyl ethyl ketone in purifying canaigre tannin. From data obtained with canaigre extract it appears that methyl ethyl ketone, saturated with water, is a highly selective solvent for separating sugars from certain tannins.

That methyl ethyl ketone saturated with water is an effective solvent, at least for canaigre tannin, is indicated by the data in Table III. Thus, in the distribution of this tannin between water and methyl ethyl ketone the solvent phase is considerably richer (approximately five fold) in tannin than the aqueous phase. In extracting concentrated aqueous solutions of canaigre tannin, one extraction suffices to remove 90% of the tannin in a high state of purity. The sugar and ash content of canaigre tannin, originally 36.4% and 4-5%, respectively, were reduced to 4.3% and 0.3% respectively by liquid-liquid extraction of the aqueous crude tannin with methyl ethyl ketone.

Methyl ethyl ketone forms an azeotrope, or constant boiling mixture, with water boiling at 73.4°C., which is very easily recovered by distillation of aqueous systems of this ketone. The azeotrope is composed of 88.7% by weight of methyl ethyl ketone and 11.3% by weight of water [9]. Thus the composition of the azeotrope is almost identical to the composition of methyl ethyl ketone saturated with water. It therefore appeared likely that this azeotrope could be satisfactorily used to leach tannins from the plant source, in a semi-continuous operation such as in a Soxhlet extractor, and perhaps give simultaneously both high purity and tannin recovery. The results in Table IV show that this was accomplished in the leaching of Chinese gallnuts, canaigre roots, and wattle bark with this azeotrope. Extracts of approximately 90% purity were obtained with extraction efficiencies ranging from 80–88%. Leaching of sumac leaves, although resulting in high tannin recovery, gave an extract of only 77% purity. Somewhat similar results were obtained with hemlock bark. Satisfactory leaching of canaigre roots by this method was only possible by conducting the process at reduced pressure (azeotrope boiled at approximately 50° C.), probably because gelatinization of the starch in the roots occurred when operated at atmospheric pressure (boiling point of azeotrope 73° C.). It is interesting to compare the leaching of wattle bark (Table IV.) and the liquid-liquid extraction of aqeous solution of wattle tannin (Table I.), with this aqeous ketone. In the former case a considerably higher tannin recovery was obtained with but a slight lowering of purity of the extract. This is in contrast to the case of hemlock bark tannin, where improved extraction efficiency is accompanied by considerably lower purity.

Summary

Methyl ethyl ketone saturated with water appears to be an example of a single organic solvent generally useful for purifying tannins. Tannins ranging from 88 to 95% purity were obtained by liquid-liquid extraction of aqeous solutions of tannins from wattle, hemlock, canaigre, quebracho, sulfited quebracho, myrobalans and gallnuts. Extracts of 70 to 80% purity were obtained from divi-divi and cube and plantation gambier.

High tannin recovery (80 to 97%) was observed in the case of canaigre, myrobalans, tannic acid, and cube and plantation gambier. Tannin recovery amounting to 40–65% resulted from wattle, quebracho, sulfited quebracho, divi-divi, and hemlock tannins. Low tannin recovery (below 20%) was observed in the case of valonia, chestnut, Borneo cutch, and mangrove extracts.

The use of methyl ethyl ketone-water azeotrope to leach tannin from sumac leaves, hemlock bark, canaigre roots, wattle bark and Chinese gallnuts (in a Soxhlet extractor) was found to give satisfactory extraction in the latter three instances, and moderately good results in the first two instances. Thus equilibrium systems of methyl ethyl ketone and water appear to have some value in purifying certain vegetable tannins.

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References

1. K. S. Kirby, E. Knowles, and T. White, *J. Soc. Leather Trades Chemists*, **35**, 338 (1951); **36**, 45, 148 (1952); **37**, 283 (1953).
2. H. Trimble, "The Tannins", J. B. Lippincott Co., Phila. (1892).
3. A. G. Perkin and A. E. Everest, "The Natural Organic Colouring Matters", Chap. XIII, Longmans, Green & Co., London (1918).

4. A. Russell, *Chem. Rev.* **17**, 155 (1935).
5. D. G. Roux, *J. Soc. Leather Trades Chemists*, **33**, 393 (1949).
6. M. A. Buchanan, H. F. Lewis and B. W. Weber, *J. Am. Leather Chemists Assoc.*., **45**, 513 (1950).
7. F. P. Luvisi, T. C. Cordon, C. W. Beebe, and J. S. Rogers, *J. Am. Leather Chemists Assoc.*, **44**, 707 (1949).
8. Am. Leather Chemists Assoc., Methods of Sampling and Analysis, 1954.
9. Technical Publication SC: 50-2, "Methyl Ethyl Ketone", 2nd Ed., Shell Chemical Corp., New York, (1950).